

RESEARCH MEMORANDUM

EFFECTS OF ADDITIVES ON CORROSION AND MASS TRANSFER IN
SODIUM HYDROXIDE - NICKEL SYSTEMS UNDER
FREE-CONVECTION CONDITIONS

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SUMMARY

A study was made of the effect of additives on the extent of corrosion and mass transfer in sodium hydroxide - "L" nickel systems. The experiments were carried out under free-convection conditions; "L" nickel crucibles half full of sodium hydroxide were heated for 24 hours at 1500° F with a temperature difference of 45° F. The extent of corrosion and mass transfer was determined by a measurement of the weight change of a specimen in the hot zone, and by metallographic examination of the specimen cross section. Additions to the melt included metals, salts, oxides, and nitrides. Reduction in mass transfer occurred with additions of powdered chromium and aluminum.

INTRODUCTION

Molten sodium hydroxide is, in many respects, an attractive choice as a high-temperature heat-transfer fluid. However, it is extremely reactive, and has produced corrosion and mass transfer in all metals or alloys which have been investigated as container materials in the temperature range 1000° to 1500° F. Of the materials studied, nickel was found to have the best resistance to intergranular attack by sodium hydroxide; however, mass transfer was experienced, that is, metal was removed from the hot zone (without intergranular penetration) and deposited in the form of crystals in the cold zone.

This investigation was conducted at the NACA Lewis laboratory to determine the feasibility of the use of additions to the melt for reduction of mass transfer in "L" nickel. For simplicity, experiments were carried out in static crucibles at 1500° F with a temperature difference of 45° F. Under these conditions, the flow is purely convective. Consequently, no account was taken of the possible effects of the higher flow rates characteristic of heat-transfer systems.

Adequate reproducibility of results in a static test was found to be dependent on several experimental conditions. Those which required careful control were composition of the crucible components, cleanliness of the crucible and specimens, atmospheric contamination of the sodium hydroxide, moisture content of the sodium hydroxide, weight of sodium hydroxide charge, and temperature conditions. Results reproducible to ± 10 percent were obtained by the use of a procedure which is described as follows:

The experiments were of 24-hours duration, and each additive was used at three different concentrations based on the weight of sodium hydroxide. The extent of corrosion and mass transfer was determined by measurement of the weight change of a nickel specimen residing in the hot zone. Metallographic examination was made of specimen cross sections in instances for which the weight changes were not conclusive.

APPARATUS AND PROCEDURE

Crucibles. - The crucibles used in this investigation were fabricated from "L" nickel tubing of the composition shown in table I. The crucibles illustrated in figure 1 were 5 inches long, with a 5/8-inch outside diameter and 1/16-inch wall thickness. The 5/16-inch diameter by 1/16-inch specimens and all of the crucible components except the vent tube were fabricated from the same length of tubing in order to insure uniform metal composition. Heliarc welding with a helium and 15-percent hydrogen atmosphere was used in fabrication. A flow of argon was maintained in the tube during welding in order to prevent oxidation of the interior of the crucibles.

Before the crucibles were assembled, the components, including the specimens, were cleaned in a modified aqua regia cleaning solution for 2 minutes (ref. 1). Sodium hydroxide of analysis shown in table II was weighed (13.0 ± 0.1 g) into the crucibles in a dry box using a nitrogen atmosphere. The tops and vent tubes were then welded into place. The moisture and air were removed by evacuation at a temperature slightly below the melting point. Evacuation and heating were continued until the pressure in the system reached 5 microns.

When evacuation was completed, a cover gas of helium was admitted. The crucibles were then transferred to the dry box and the additives to be tested were placed into the crucibles through the vent tubes. The dry box atmosphere was then removed by evacuation and a fresh supply of cover gas at 2 pounds per square inch gage was admitted. Crimping and welding at the crimp served to seal the crucibles. Thermocouples were attached at the liquid level, $2\frac{1}{2}$ inches from the bottom, and at a point 1/8 inch from the bottom. The crucibles were then ready for mounting in the holder as shown in figure 2.

Apparatus. - A specially designed furnace, illustrated in figure 3, was used to obtain the uniform temperature conditions which had been found necessary to achieve reproducible results. The maximum temperature difference between any two crucibles at any height was less than 10° F, and the temperature difference from bottom to liquid level was $45^{\circ} \pm 5^{\circ}$ F. In order to insure uniformity in temperature conditions, the crucible holder was always mounted in the same position in the furnace.

Test procedure. - The four crucibles mounted in the crucible holder were lowered into the furnace which had been stabilized at 1500° F. After a period of 24 hours, the crucible holder was removed and the assembly allowed to cool in air. The crucibles were opened with a tubing cutter, and the appearance of the sodium hydroxide and crucible interior was noted. The caustic was then removed by solution in a stream of hot water. The crucibles and specimens were rinsed with acetone and dried, and the specimen weights were redetermined.

The specimen weight loss was previously shown (ref. 2) to provide an adequate measure of the extent of mass transfer in a nickel crucible containing only sodium hydroxide. However, when additions to the sodium hydroxide caused reactions leading to intergranular penetration, corrosion layer formation, and/or the deposition of metallic films on the specimens, the specimen weight changes alone could not be relied upon as an adequate criterion for the measurement of mass transfer. Consequently, specimens which showed a smaller weight loss than the control or a weight increase were examined metallographically and these results were also tabulated.

A test using four crucibles containing no additions to the melt was used to determine the degree of reproducibility of the experiment. In addition, a control crucible containing no additive was included in each set.

RESULTS AND DISCUSSION

Reproducibility. - Table III lists the results of a typical experiment used to determine the degree of reproducibility. A mean weight loss of 5.1 milligrams was obtained for the four specimens. The average deviation for a single observation was ± 8.2 percent in this experiment. When data for the control specimens were combined, an average deviation of ± 9.8 percent was obtained.

Appearance of specimens. - The control specimens and those for which the additive was inert or caused an increase in rate of surface metal removal were bright and shining in appearance. In cases in which metal deposition, corrosion layer formation, and intergranular penetration occurred, the specimens were dull. A nonmetallic coating was visible in several instances.

For the sake of brevity, the discussion of the additives is included in the remarks column of the tables.

Additives having a detrimental effect. - The results for the additives considered detrimental are given in table IV, together with the experimental conditions. Additives were listed as detrimental if their use resulted in increased specimen weight loss, specimen weight gain, or intergranular penetration.

Additives having no marked effect (inert). - The additives listed in table V caused no marked change in specimen weight loss. Table V contains, in addition to the inert additives, data obtained by the use of caustic with low carbonate content and that obtained under vacuum.

Additives having beneficial effects. - Additives were considered beneficial if they caused a reduction in specimen weight loss or if a small specimen weight gain could be accounted for by a surface coating on the specimen.

Of all the additives tested, only chromium and aluminum (table VI) proved beneficial. A study of the photomicrographs (also discussed in the tables) indicated that chromium and aluminum additions reduced the attack on the nickel and apparently caused the formation of a very thin film on the surface of the specimens.

SUMMARY OF RESULTS

Under experimental conditions which proved to give reproducible results, an investigation was carried out to determine the effects of various additives on corrosion and mass transfer in static nickel crucibles containing molten sodium hydroxide at 1500° F with a temperature difference of 45° F.

The results of this investigation can be summarized as follows:

1. Additives considered detrimental in that they caused an increase in the weight loss, a marked weight gain, or intergranular penetration of the specimens, were palladium, zinc, platinum, aluminum oxide, iron, cobalt, calcium, sodium, iodine, carbon, sodium chromate, potassium chromate, cobaltic oxide, ferric oxide, sodium peroxide, and sodium phosphate.
2. Additives which caused no marked change or a very small change in the weight loss of the specimens and therefore were considered to be inert were copper, silver, gold, columbium nitride, and tantalum nitride. The absence of a cover gas or the use of purified sodium hydroxide had no marked effect on the weight change of the specimens.

3. Additives which reduced the weight loss of the specimens and were considered beneficial were aluminum and chromium.

Lewis Flight Propulsion Laboratory
National Advisory Committee for Aeronautics
Cleveland, Ohio, May 21, 1954

REFERENCES

1. Anon.: Metals Handbook, 1948 ed. Am. Soc. Metals (Cleveland), 1948, p. 1041, formula 3.
2. Mosher, Don R., and Lad, Robert A.: Kinetic Study of Mass Transfer by Sodium Hydroxide in Nickel Under Free-Convection Conditions. NACA RM E53K24, 1954.

TABLE I. - COMPOSITION OF "L" NICKEL TUBING

Material	Percent ^a
Manganese	0.149 $\pm$ 0.015
Iron	.059 $\pm$.006
Copper	.028 $\pm$.006
Carbon	.024 $\pm$.005
Silicon	.020 $\pm$.002
Sulfur	.008 $\pm$.001
Cobalt	.119 $\pm$.013
Nickel	Balance

^aAverage of analyses of all lengths of tubing used.

TABLE II. - ANALYSIS OF SODIUM HYDROXIDE PELLETS

[Eimer and Amend, lot 502875, c.p. grade.]

Material	Percent ^a
Sodium hydroxide	97.6
Chloride (Cl)	0.005
Iron (Fe)	.001
Other heavy metals (as Ag)	0
Carbonate (Na_2CO_3)	.32
Phosphate (PO_4)	0
Silica and ammonium hydroxide precipitate	0
Total nitrogen (as NH_3 , NO_2)	.001
Sulfate (SO_4)	0

^aAs per label and verified by analysis at time of use.

TABLE III. - REPRODUCIBILITY

Temperature, °F		Specimen weight change, mg
Bottom of crucible	Liquid level	
1535	1491	-4.3
1534	1488	-5.2
1530	1489	-5.8
1533	1489	-5.0
Mean		-5.1

TABLE IV. - ADDITIVES HAVING A DETRIMENTAL EFFECT

Additive		Temperature, °F		Specimen weight change, mg	Remarks
Material	Percent	Bottom of crucible	Liquid level		
Pd	0	1539	1510	-5.3	Visual examination of mass-transfer deposit on crucible wall indicated decrease in transfer. Increase in specimen weight loss was found to be the result of formation of a Pd-Ni alloy.
Pd	1	1539	1510	-8.5	
Pd	3	1539	1508	-16.9	
Pd	5	1534	1504	-17.5	
Zn	0	1539	1497	-4.4	Metallographic studies of specimens which gained weight showed a coating of zinc metal (cause of weight gain) and slight intergranular attack illustrated by photomicrograph of fig. 4(c).
Zn	1	1549	1510	-12.4	
Zn	3	1523	1489	29.6	
Zn	5	1530	1490	120.7	
Pt	0	1539	1501	-5.8	Deposition in the cold zone was in accordance with increased specimen weight loss.
Pt	1	-----	-----	-----	
Pt	3	1546	1497	-42.5	
Pt	5	1532	1494	-29.0	
Al ₂ O ₃	0	1539	1482	-5.5	Specimens which gained weight were subjected to metallographic examination. The photomicrograph illustrated in fig. 4(d) shows random removal of surface nickel much like that of a control specimen (fig. 4(b)). Cause of weight gain of these specimens is not known.
Al ₂ O ₃	1	1544	1485	1.2	
Al ₂ O ₃	3	1536	1472	.3	
Al ₂ O ₃	5	1534	1469	-.9	
Fe	0	1539	1480	-6.5	
Fe	1	1537	1480	-25.7	
Fe	3	1534	1472	-28.4	
Fe	5	1527	1466	-28.1	
Co	0	1539	1484	-4.5	Specimens were observed to have a coated appearance on upper surface. Calculations indicate that this coating, which is illustrated in photomicrograph of fig. 4(e), is sufficient to cause the weight gain observed.
Co	1	1546	1491	.6	
Co	3	1549	1487	7.2	
Co	5	1534	1475	8.2	
Ca	0	1539	1482	-5.0	Photomicrograph of fig. 4(f) shows that specimens underwent some intergranular attack. When intergranular penetration takes place, weight change of specimens cannot be relied upon to determine effect of additive on corrosion and mass transfer.
Ca	.25	1535	1480	-10.0	
Ca	.55	1517	1470	-9.9	
Ca	.60	1525	1473	-2.8	
Ca	0	1539	1486	-5.6	
Ca	1	1539	1489	-14.9	
Ca	3.2	1516	1467	-10.2	
Ca	3.5	1534	1468	.4	
Na	0	1539	1491	-4.4	
Na	1	1541	1491	-24.2	
Na	1.25	1526	1481	-35.1	
Na	1.5	1534	1485	-61.1	
I ₂	0	1539	1487	-6.3	Specimens were coated.
I ₂	1	1545	1491	-22.7	
I ₂	3	1523	1473	-17.0	
I ₂	5	1525	1471	-22.9	
C	0	1539	1488	-4.9	When the crucibles containing carbon were washed out, large amounts of gas evolution was observed. Specimens were coated.
C	1	1545	1489	-78.6	
C	3	1536	1478	-8.5	
C	5	1539	1477	-7.8	
Co ₂ O ₃	0	1539	1487	-5.2	A black residue of unknown composition adhered to underside of specimens. This residue became thicker as amount of cobaltic oxide was increased. Photomicrograph of upper surface (fig. 4(g)) indicated random removal of surface nickel.
Co ₂ O ₃	1	1546	1494	-19.8	
Co ₂ O ₃	3	1532	1479	-.5	
Co ₂ O ₃	5	1532	1479	11.1	
Fe ₂ O ₃	0	1539	1482	-5.4	Specimens had a coating of varying thickness on upper surface. Coating did not appear to be same as that found in other additive runs. The inconsistency of results may be due to variation of coatings.
Fe ₂ O ₃	1	1535	1485	-9.2	
Fe ₂ O ₃	3	1531	1474	-11.1	
Fe ₂ O ₃	5	1537	1474	-4.8	
Fe ₂ O ₃	0	1539	1489	-6.9	
Fe ₂ O ₃	5	1537	1483	-7.2	
Fe ₂ O ₃	7	1530	1474	-20.7	
Fe ₂ O ₃	10	1537	1476	-13.8	
Na ₂ O ₂	0	1539	1489	-5.3	A black residue of unknown composition adhered to the bottom of specimens.
Na ₂ O ₂	1	1544	1493	-22.5	
Na ₂ O ₂	3	1530	1482	-11.8	
Na ₂ O ₂	5	1534	1484	-19.3	
Na ₂ CrO ₄ ·4H ₂ O	0	1539	1487	-5.1	Specimens were coated on upper surface. ^a
Na ₂ CrO ₄ ·4H ₂ O	1	1539	1488	-18.4	
Na ₂ CrO ₄ ·4H ₂ O	3	1531	1480	-26.1	
Na ₂ CrO ₄ ·4H ₂ O	5	1533	1481	-21.6	
K ₂ CrO ₄	0	1539	1485	-6.3	Specimens were coated on upper surface. ^a
K ₂ CrO ₄	1	1539	1488	-20.7	
K ₂ CrO ₄	3	1526	1478	-20.6	
K ₂ CrO ₄	5	1526	1477	-19.6	
Na ₃ PO ₄ ·12H ₂ O	0	1539	1492	-5.3	(This run might be classified inert.) ^a
Na ₃ PO ₄ ·12H ₂ O	1	1542	1495	-5.4	
Na ₃ PO ₄ ·12H ₂ O	(b)	1537	1485	-5.2	
Na ₃ PO ₄ ·12H ₂ O	5	1537	1488	-8.6	

^aAdded before purging to remove water of crystallization.^bAmount added not accurately known.

TABLE V. - ADDITIVES HAVING NO MARKED EFFECT

Additive		Temperature, °F		Specimen weight change, mg	Remarks
Material	Percent	Bottom of crucible	Liquid level		
Cu	0	1539	1500	-5.8	
Cu	1	1545	1504	-8.4	
Cu	3	1539	1497	-6.7	
Cu	5	1537	1491	-5.8	
Ag	0	1539	1495	-5.8	
Ag	1	1542	1493	-6.0	
Ag	3	1539	1491	-4.8	
Ag	5	1533	1487	-5.1	
Au	0	1539	1493	-5.8	
Au	1	1546	1497	-6.5	
Au	3	1533	1487	-5.8	
Au	5	1530	1480	-6.3	
CbN	0	1539	1487	-5.3	
CbN	1	1542	1491	-5.8	
CbN	3	1527	1480	-5.6	
CbN	5	----	----	---	
TaN	0	1539	1482	-5.4	
TaN	1	1541	1484	-6.3	
TaN	3	1530	1473	-6.9	
TaN	5	1514	1467	-8.4	
Control		1539	1488	-6.4	Crucibles in this run were crimped while still under vacuum, and no cover gas was admitted to them.
No cover gas		1538	1490	-6.7	
No cover gas		1529	1480	-4.8	
No cover gas		1521	1480	-4.6	
Control		1539	1491	-6.0	It is known that additions of sodium carbonate cause increase in weight loss of specimens. Therefore, these runs were made using purified sodium hydroxide (0.05 percent Na_2CO_3) to determine effect of reducing the carbonate content.
13g Purified NaOH		1540	1493	-6.3	
13g Purified NaOH		1528	1480	-4.7	
13g Purified NaOH		1523	1480	-5.6	
Control		1539	1495	-6.6	The results indicate that reducing the carbonate content had no marked effect.
13g Purified NaOH		1539	1493	-7.0	
13g Purified NaOH		1530	1492	-5.7	
13g Purified NaOH		1534	1479	-5.5	

TABLE VI. - ADDITIVES HAVING A BENEFICIAL EFFECT

Additive		Temperature, °F		Specimen weight change, mg	Remarks
Material	Percent	Bottom of crucible	Liquid level		
Cr	0	1539	1495	-5.0	Although chromium was originally believed to be detrimental, metallographic studies of a specimen showed no noticeable removal of surface nickel when compared to control specimen (fig. 4(b)) and specimen which did not come in contact with molten sodium hydroxide (fig. 4(a)). Visual examination of specimens revealed a coated appearance on upper surface. It is believed that this coating, although not visible in the photomicrograph of fig. 4(h), is the cause of weight gain observed.
	1	1547	1499	2.4	
Cr	3	1546	1493	2.9	
Cr	5	1542	1489	1.3	
Al	0	1539	1495	-6.3	Only crucibles containing small amounts of aluminum could be evaluated. Crucibles which contained larger amounts of aluminum leaked at a weld during runs. This may have been caused by high pressure of the gas evolved during reaction of aluminum with sodium hydroxide. Comparison of photomicrographs of figs. 4(a), (b) and (i) shows no noticeable corrosion in the case of aluminum additive.
	1	1543	1498	-.5	
Al	3	----	----	---	
Al	5	----	----	---	
Al	0	1539	1481	-4.8	
	1	1546	1484	-1.1	
Al	3	----	----	---	
Al	5	----	----	---	
Al	0	1539	1494	-5.3	
	1.2	1532	1509	-1.0	
Al	3.35	----	----	---	
Al	5.45	----	----	---	

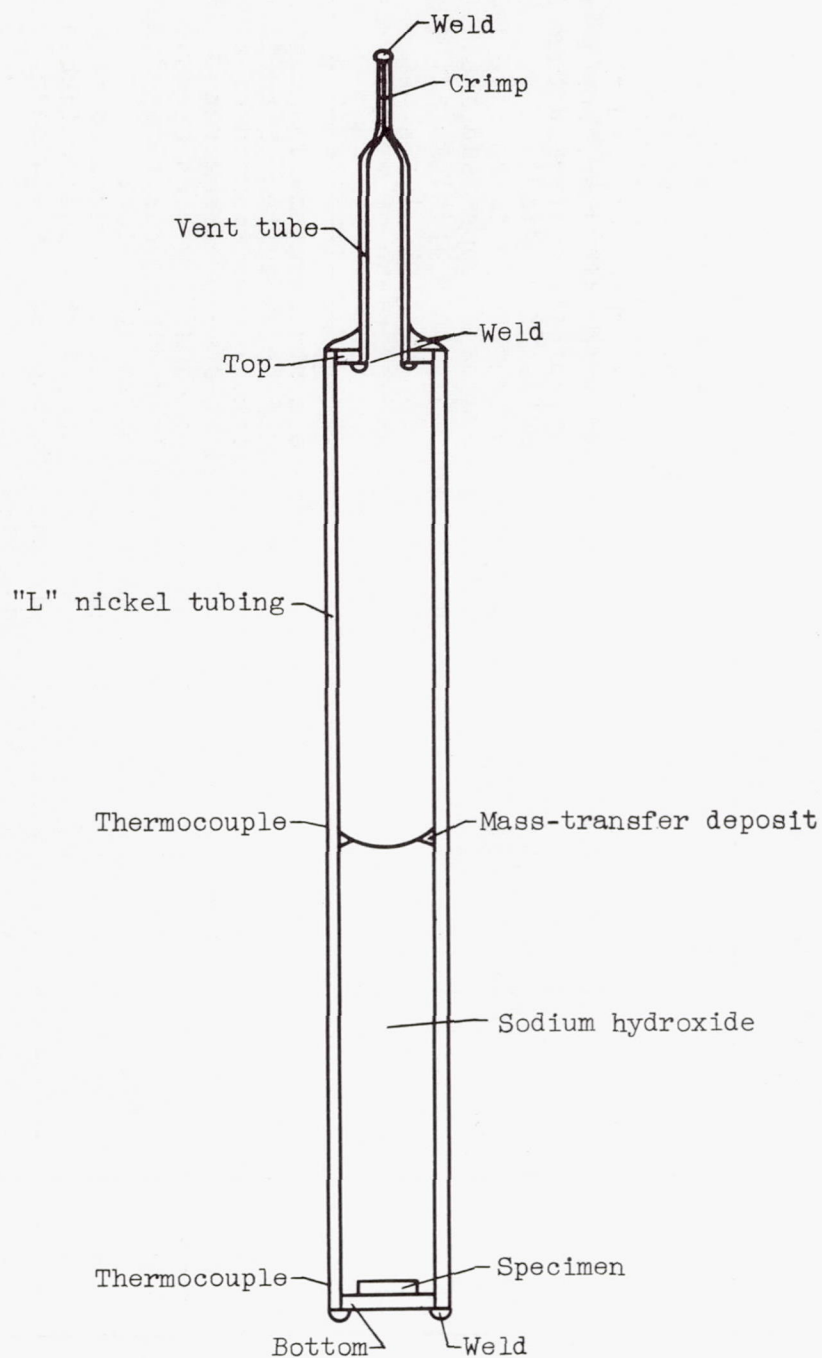


Figure 1. - Static crucible.

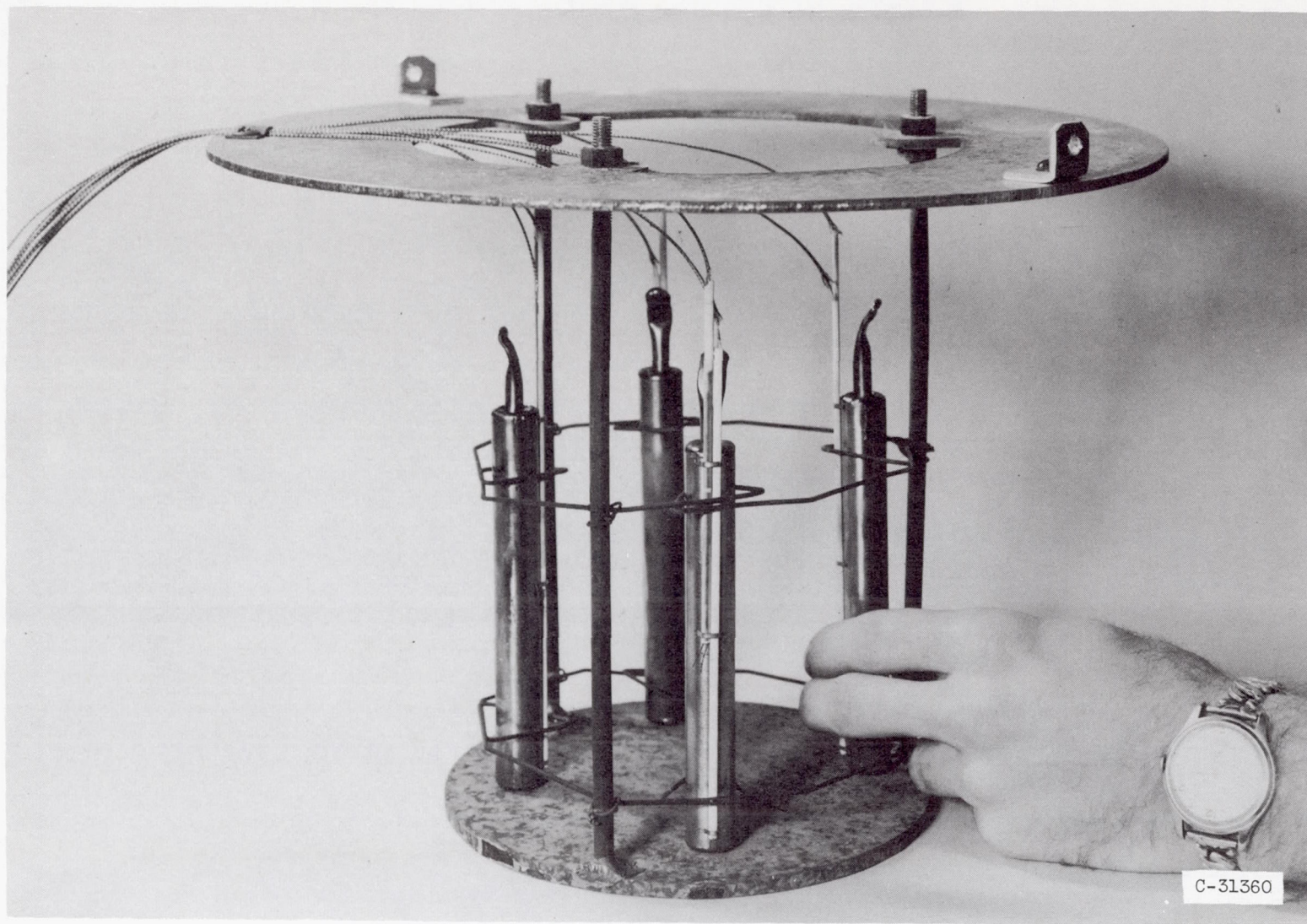


Figure 2. - Crucible holder with crucibles in position.

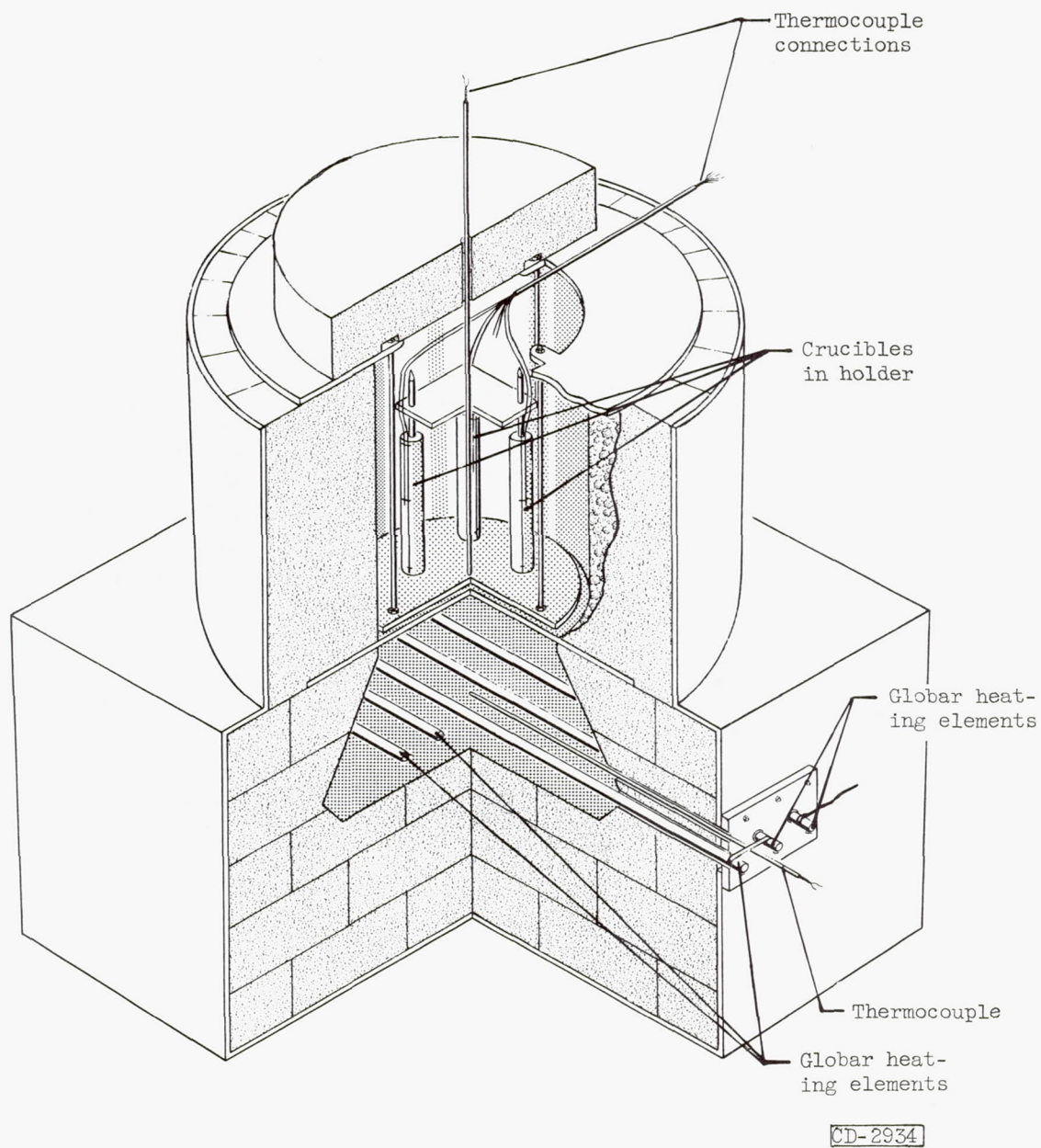
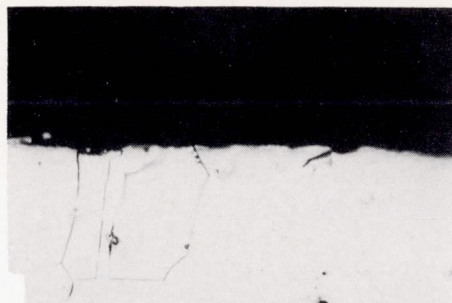
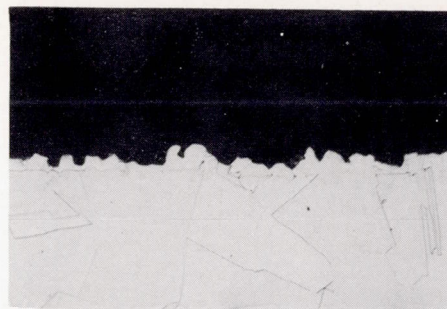


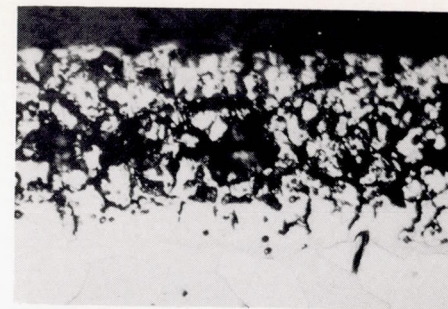
Figure 3. - Crucible furnace.



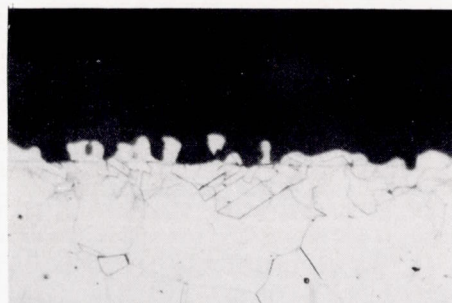
(a) Before test.



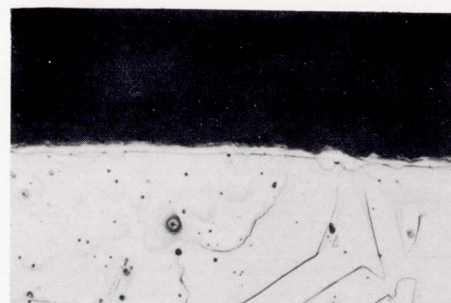
(b) Control, no addition.



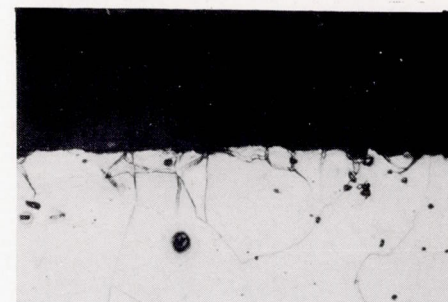
(c) Zinc addition, 3 percent.



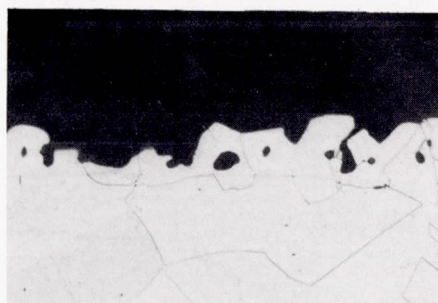
(d) Alumina addition, 1 percent.



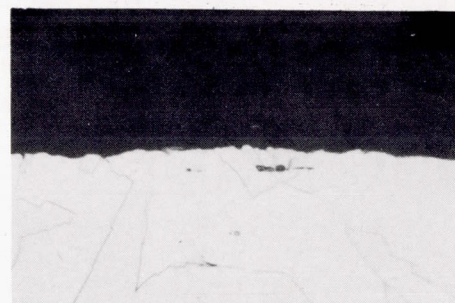
(e) Cobalt addition, 5 percent.



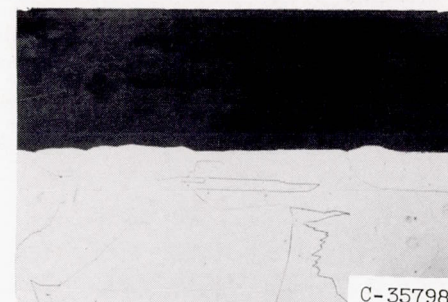
(f) Calcium addition, .6 percent



(g) Cobaltic oxide addition, 5 percent.



(h) Chromium addition, 5 percent.



(i) Aluminum addition, 1 percent.

Figure 4. - Photomicrographs of upper surface of nickel specimens at X250.